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<u>L5</u>	L4 AND (anaerob\$4 SAME (alkali OR sodium OR potassium OR calcium))	15	<u>L5</u>
<u>L4</u>	L3 AND (acrylate OR methacrylate OR (meth ADJ acrylate))	62	<u>L4</u>
<u>L3</u>	L2 AND (peroxide AND (sulfimide OR saccharin OR benzosulfimide))	62	<u>L3</u>
<u>L2</u>	L1 AND (alkali OR sodium OR potassium OR calcium OR (alkaline ADJ earth))	302	<u>L2</u>
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L5: Entry 1 of 15

File: USPT

Oct 10, 1995

DOCUMENT-IDENTIFIER: US RE35058 E

TITLE: Peroxy cured (meth)acrylic ester compositions employing nitrite, borate, silicate or carbonate salt accelerators

Brief Summary Text (2):

(Anaerobic formulations, i.e. (meth)acrylic ester formulations which are oxygen stabilized and cure as a result of oxygen deprivation,) have become well known since their disclosure in U.S. Pat. No. 2,628,178. The invention of formulations employing hydroperoxide catalysts which are stable without aeration which was disclosed in U.S. Pat. No. 2,895,950 (Kriebel) prompted a wide range of commercial uses for such formulations including thread locking, impregnation of porous articles, gasketing and adhesive bonding applications. Acceleration of the cure of such composition has been disclosed in numerous patents. (Sulfimide accelerators, particularly saccharin (benzoic sulfimide),) have been used in most anaerobic formulations since the disclosure of their utility in U.S. Pat. No. 3,046,262. Other accelerator systems which are known for use in anaerobic formulations include various amine compounds as disclosed, for instance, in U.S. Pat. Nos. 3,041,322, 3,203,941 and 3,218,305 and various compounds having structures analogous to sulfimides such as disclosed in U.S. Pat. No. 4,513,127 and U.S. Pat. No. 4,622,348 and the references disclosed therein. Certain acyl hydrazine compounds are disclosed as anaerobic accelerators in U.S. Pat. Nos. 4,180,640 and 4,287,330 preferably in combination with an acid having a small pKa of 6 or less. The various known types of accelerators are often used in combination in commercial formulations.

Brief Summary Text (5):

It has also (long been known) that transition metals, especially copper or iron, play an important part in the cure mechanism of peroxide initiated acrylic formulations. This is especially so in anaerobic cure mechanisms. Transition metal oxidation is often part of the redox reaction which produces free radicals from peroxy initiators. Transition metal may be supplied by the substrate itself or in the form of salts of metals incorporated into the formulation or applied to the substrate. Copper, manganese, iron, cobalt and vanadium salts are all known for this purpose, copper and iron being the most commonly used. In impregnation processes which employ aeration of the acrylic monomer formulation it is typical to add 1-10 ppm copper as a copper salt directly to the formulation. As disclosed in U.S. Pat. No. 4,632,945, combinations of copper and iron salts or complexes may also be employed.

Brief Summary Text (12):

provided that if the composition includes an acid having a pKa of 6 or less, the composition further includes at least 1 ppm of a transition metal salt and is free of compounds of the formula: ##STR1## where R.sup.1 is a monovalent hydrocarbon group, x is an integer of at least 1 and R.sup.2 is H or a x-valent hydrocarbon group. Subject to the restrictions above, the composition may also include other conventional accelerators such as sulfimide, phenyl hydrazide and amine accelerators.

Brief Summary Text (19):

A still further aspect of the invention comprises an improved process for bonding a pair of substrates with an anaerobic adhesive formulation by applying the adhesive between the substrates and joining them until bonded, the improvement comprising first (determining whether either of the substrates has been treated with a composition leaving a residue of a nitrite, silicate, borate, or alkaline carbonate salt and if so, selecting an anaerobic adhesive for application to the substrates which is free of an acid having a pKa of 6 or lower.)

Detailed Description Text (4):

One class of monomers suited for use in this invention comprises acrylate esters having

the following general formula: ##STR3## wherein R.sup.4 represents a radical selected from the group consisting of hydrogen, halogen, alkyl of 1-4 carbon atoms, inclusive, hydroxy alkyl of 1-4 carbon atoms inclusive, and ##STR4## R.sup.3 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of 1-4 carbon atoms; R.sup.5 is a radical selected from the group consisting of hydrogen, --OH and ##STR5## m is an integer equal to at least 1, e.g. from 1 to 8 or higher, for instance, from 1 to 4 inclusive, n is an integer equal to at least 1, for example, 1 to 20 or more; and p is 0 or 1.

Detailed Description Text (6):

In addition to the monomers described above, epoxy acrylate monomers (i.e. the reaction products of epoxy compounds or prepolymers with acrylic or methacrylic acids) and urethane acrylate capped prepolymers such as those described in U.S. Pat. Nos. 4,309,526, 4,295,909, 4,018,851, 4,380,613, and 4,439,600 may be employed. Also useful are (meth)acrylic esters of ethoxylated bisphenol A and structurally similar compounds.

Detailed Description Text (7):

Although di-and and other poly(meth)acrylate esters are preferred, monoacrylate esters can be used, particularly if the non-acrylate portion of the ester contains a hydroxyl or amino group, or other reactive substituent which serves as a site for potential cross-linking. Examples of useful mono(meth)acrylate monomers are hydroxyethyl methacrylate, cyanoethyl acrylate, t-butylaminoethyl methacrylate, glycidyl methacrylate, dicyclopentadiene methacrylate, lauryl acrylate and lauryl methacrylate. Further details on useful monomers may be found in U.S. Pat. No. 4,287,330 at Col. 3, line 51-Col. 6, line 44.

Detailed Description Text (8):

Silicones having (meth)acrylate ester functionally are another class of monomers which may be used in the invention. Examples of such silicones may be found in U.S. Pat. Nos. 3,878,263, 4,035,355, 4,348,454, 4,477,326, 4,503,208, 4,504,629, 4,575,545, 4,575,546, 4,640,940, and 4,684,538, all incorporated herein by reference.

Detailed Description Text (11):

The preferred compositions include at least one monomer or prepolymer which is characterized by at least two acrylate or methacrylate groups per molecule. Such compounds are suitably used at levels of 30% or more by weight of the composition. The improved thermal properties of the inventive compositions are usually most striking when the formulation contains a urethane acrylate or urethane methacrylate capped prepolymer.

Detailed Description Text (12):

The compositions of the inventions cure via a peroxy initiated free radical mechanism. Useful initiators are any of a wide variety of known peroxy compounds. Illustrative of such initiators are the diacyl peroxides such as benzoyl peroxide; dialkyl peroxides such as di-t-butyl peroxide; ketone peroxides such as methylethyl ketone peroxides; peresters which readily hydrolyze, e.g., t-butyl peracetate, t-butylperbenzoate, di-t-butylperphthalate; and peroxycarbonates, i.e., reaction products of isocyanates and hydroperoxides. A particularly useful class of peroxy initiators are the organic hydroperoxides such as cumene hydroperoxide, methyl ethyl ketone hydroperoxide, t-butyl hydroperoxide, etc. Of these, cumene hydroperoxide is especially preferred. It is also known in the art to generate hydroperoxides in-situ by aeration of some (meth)acrylic ester monomers. The peroxy initiators should be used at a concentration of about 0.01% to about 10% by weight of the total formulation, preferably 0.1% to about 5% by weight, most preferably about 1%-3% by weight.

Detailed Description Text (14):

As previously mentioned, the inventive compositions also include an accelerating salt selected from nitrite, borate, silicate and alkaline carbonate salts. Most preferred are the nitrite salts as they show the highest acceleration activity. The counter-ion is not considered critical. Suitably these salts are alkali metal salts such as sodium, potassium, or lithium salts. Such salts are commonly used in metal corrosion inhibition formulations. Other counter-ions, however, may be useful such as ammonium or copper salts.

Detailed Description Text (15):

The level of accelerating salt may be very low. For surface activation, levels of sodium nitrite based corrosion inhibitor providing just a few ppm nitrite ion on the surface can be sufficient to substantially improve the cure rate. When added to

adhesive and sealant compositions, the level is generally recommended to be between 0.001 and 5.0 percent, preferably 0.01 and 1.0 percent, more preferably between 0.1 and 0.5 percent.

Detailed Description Text (16):

Other accelerators of anaerobic polymerization may also be advantageously included. Such accelerators include a variety of secondary and tertiary organic amines as well as sulfimides (e.g. benzoic sulfimide) which are also known in the art. These may be used at a concentration range of about 0.1 to about 5, preferably about 1 to about 2% by weight of the total composition. However, it has been found that certain combinations of accelerators have the opposite effect in the presence of the accelerating salt so that polymerization of the composition is severely inhibited. If compounds having a pKa of less than 6 are present in the formulation the presence of a nitrite, borate, silicate or alkaline carbonate salt in the formulation or on the substrate will usually substantially inhibit cure speed. The inhibition effect is magnified if the formulation includes both an acid having an pKa of 6 or less and a compound of the formula: ##STR6##

Detailed Description Text (22):

Model anaerobic formulations were prepared as in Table 1. Cure rates of the respective formulations between a sodium chloride salt plate and a polished aluminum panel (having a trace content of copper) were monitored for two hours by real time FTIR and compared to the cure rate observed when the aluminum panel was treated by immersing it in a 5 wt % solution of aqueous sodium nitrite for 15 minutes and blow drying the panel with dry nitrogen immediately after removing it from the solution. The highest observed cure rate and percent cure after 2 hours for the respective formulations on untreated and treated panels are recorded in Table I below.

Detailed Description Text (28):

Several ppm of copper (II) salt was added together with the acrylic acid and/or sodium nitrite additives as shown in Table III. Oxygen was bubbled through the respective formulations and samples rested for 40.degree. C. gel times after 1 hour and 24 hour aging periods. The results, given in Table III demonstrate that in this system acrylic acid alone had an inhibiting effect whereas the nitrite alone gave substantial acceleration which was not significantly affected when combined with small amounts of acrylic acid. At higher levels of acrylic acid, a synergistic acceleration was observed.

Detailed Description Paragraph Table (1):

TABLE I										Compositions (parts by wt.) Ingredients									
A	B	C	D	E	F														
92.1	92.1	92.1				dimethacrylate	Cumene	hydroperoxide	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
0.8	0.8	0.8	--	--	--	Acrylic acid	--	4.3	--	4.3	4.3	--	Acetyl	phenyl	hydrazine	0.6	0.6		
--	0.6	--	--	--	--	% Cure	2 hrs	60	77	36	65	35	16	untreated	% Cure	2 hrs	72	17	34
						NaNO.sub.2	treated	Untreated	highest	cure	0.10	0.27	0.21	0.08	0.02	0.02	rate		
						(moles/l-sec)	NaNO.sub.2	treated	highest	0.62	0.02	0.11	0.01	0.01	0.16	cure	rate		
						(moles/l-sec)													

Detailed Description Paragraph Table (3):

CLAIMS:

(a) at least one (meth)acrylic ester;

(b) a polymerization initiating effective amount of a peroxy compound; and

(c) an effective amount for accelerating polymerization of a nitrite, borate, silicate or alkaline carbonate salt,

provided that if the formulation includes an acid having a pKa of 6 or less, the formulation further includes at least 1 ppm of a transition metal salt and is free of compounds of the formula: ##STR7## where R^{sup.1} is a monovalent hydrocarbon group, x is an integer of at

least 1 and R.sup.2 is H or a x-valent hydrocarbon group.]. 2. A formulation as in claim .[.1.]. .Iadd.12, 14 or 15 .Iaddend.wherein the

(meth)acrylic ester comprises at least two (meth)acrylic groups. 3. A formulation as in claim g .[.1.]. .Iadd.12 or 14 .Iaddend.wherein the

transition metal salt is a salt of copper, iron or mixtures thereof. 4. A formulation as in claim .[.1.]. .Iadd.12, 14 or 15 .Iaddend.adapted to be

anaerobically curable. 5. A formulation as in claim .[.1.]. .Iadd.12, 14, or 15 .Iaddend.wherein the peroxy compound is a hydroperoxide or perester.

. A formulation as in claim .[.4.]. .Iadd.14 .Iaddend.wherein the

formulation is adapted for impregnation into a porous substrate. 7. A formulation as in claim .[.1.]. .Iadd.12 or 15 .Iaddend.wherein the

ingredient (c) is a nitrite salt. 8. A formulation as in claim 7 wherein

the nitrite salt is a nitrite salt of an alkali metal. 9. A formulation as in claim .[.1.]. .Iadd.12, 14 or 15 .Iaddend.wherein the ingredient (c) is

present in an amount between 0.001% and 5.0%. 10. A formulation as in claim .[.1.]. .Iadd.12, 14 or 15 .Iaddend.further comprising between about

0.1% and 5% of a sulfimide accelerator. 11. A formulation as in claim .[.1.]. .Iadd.14 .Iaddend.which is substantially free of an acid having a

pKa of 6 or less. .Iadd.12. A substantially 100% solids curable formulation comprising:

(a) at least one (meth)acrylic ester;

(b) a polymerization initiating effective amount of a peroxy compound; and

(c) an effective amount for accelerating polymerization of a nitrite, borate, silicate or alkaline carbonate salt,

provided that the composition includes an acid having a pKa of 6 or less, and the composition further includes at least 1 ppm of a transition metal salt and is free of compounds of the formula: ##STR8## where R.sup.1 is a monovalent hydrocarbon group, x is an integer of at least 1 and R.sup.2 is H or a x-valent hydrocarbon group. .Iaddend.

.Iadd. 3. A formulation as in claim 12 wherein said acid is acrylic acid.

.Iaddend. .Iadd.14. A substantially 100% solids curable formulation comprising:

(a) at least one (meth)acrylic ester;

(b) a polymerization initiating effective amount of a peroxy compound; and

(c) an effective amount for accelerating polymerization of a borate, silicate or alkaline carbonate salt,

provided that if the composition includes an acid having a pKa of 6 or less, the composition further includes at least 1 ppm of a transition metal salt and is free of compounds of the formula: ##STR9## where R.sup.1 is a monovalent hydrocarbon group, x is an integer of at least 1 and R.sup.2 is H or a x-valent hydrocarbon group. .Iaddend.

.Iadd. 5. A substantially 100% solids curable formulation comprising:

(a) at least one (meth)acrylic ester;

(b) a polymerization initiating effective amount of a peroxy compound; and -

(c) an effective amount for accelerating polymerization of a nitrite, borate, silicate

or alkaline carbonate salt,

provided that the composition is substantially free of an acid having a pKa of 6 or less, and further comprises a co-accelerator compound of the formula: ##STR10## where R.sup.1 is a monovalent hydrocarbon group, x is an integer of at least 1 and R.sup.2 is H or a x-valent hydrocarbon group. .Iaddend.

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File: USPT

Apr 14, 1981

DOCUMENT-IDENTIFIER: US 4262106 A

TITLE: Highly stable anaerobic compositions and process for preparing them

Brief Summary Text (2):

Polymerizable anaerobic compositions are precatalyzed polymerizable compositions which cure by a polymerization process which is inhibited by oxygen. As a result they remain in an unpolymerized state as long as adequate contact is maintained with air or other oxygen-bearing materials. Cure may be instituted by removing the composition from contact with oxygen. Since such oxygen free conditions can be found between closely fitting, non-porous surfaces, such as between interfitting metal parts, anaerobic compositions have found great utility in the adhesives and sealants fields.

Brief Summary Text (16):

The most desirable monomers for use in anaerobic systems are polymerizable acrylate esters. When used in the process of this invention, preferably at least a portion of the acrylate monomer is a di- or other polyacrylate ester. These poly-functional monomers produce cross-linked polymers, which serve as more effective and more durable sealants and adhesives, the most common uses for the anaerobic compositions.

Brief Summary Text (17):

The most highly preferred acrylate esters which can be used in the compositions disclosed herein are polyacrylate esters which have the following general formula: ##STR1## wherein R.sup.1 represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxy alkyl of from 1 to about 4 carbon atoms, and ##STR2## R.sup.2 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R.sup.3 is a radical selected from the group consisting of hydrogen, hydroxyl, and ##STR3## m is an integer equal to at least 1, e.g., from 1 to about 15 or higher, and preferably from 1 to about 8 inclusive; n is an integer equal to at least 1, e.g., 1 to about 20 or more, and preferably between about 2 and about 6; and p is one of the following: 0, 1.

Brief Summary Text (19):

While di- and other polyacrylate esters--and particularly the polyacrylate esters discribed in the preceding paragraphs--have been found particularly desirable, monofunctional acrylate esters (esters containing one acrylate group) also may be used. When dealing with monofunctional acrylate esters, it is preferable to use an ester which has a relatively polar alcoholic moiety. Such materials are less volatile than low molecular weight alkyl esters and, more important, the polar group tends to provide intermolecular attraction in the cured polymer, thus producing a more durable sealant or adhesive. Most preferably the polar group is selected from the group consisting of labile hydrogen, heterocyclic ring, hydroxy, amino, cyano, and halogen polar groups. Typical examples of compounds within this category are cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, and chloroethyl methacrylate.

Brief Summary Text (20):

Other acrylates can be used in the anaerobic compositions, such as the isocyanate-monoacrylate reaction products described in the above mentioned U.S. Pat. No. 3,425,988. However, when other acrylates are used, they preferably are used in combination with one or more members from either or both of the above described classes of polyacrylate and monoacrylate monomers. Most preferably, polyacrylates having the chemical formula (1), given above, comprise at least about fifty percent by weight of the acrylates used since these monomers have been found clearly superior in anaerobic sealants, as is more fully described below.

Brief Summary Text (21):

An indicated above the anaerobic compositions as discussed herein are prepared by mixing a hydroperoxide catalyst with one or more acrylate esters as described above. Hydrogen-peroxide may be used, but the most desirable polymerization initiators are the organic hydroperoxides. Included within this definition are materials such as organic peroxides or organic peresters which decompose or hydrolyze to form organic hydroperoxides in situ. Examples of such peroxides and peresters are cyclohexyl hydroxycyclohexyl peroxide and t-butyl perbenzoate, respectively.

Brief Summary Text (23):

Other materials can be added to the mixture of polymerizable monomer and latent polymerization initiator, such as quinone or polyhydric phenol stabilizers, thickeners, plasticizers, dyes, adhesive agents, thixotropic agents, etc. Such materials can be used in such combinations and proportions as is desired, provided they do not affect adversely the anaerobic nature of the composition. These materials generally do not comprise more than about 50 percent by weight of the total composition, and preferably not more than about 20 percent by weight of the composition.

Brief Summary Text (31):

Another highly successful class of accelerators is the organic sulfimides, i.e., organic compounds which contain the group ##STR4## Because of the extreme effectiveness of the sulfimides as accelerators for anaerobic compositions, and because of the apparent strong interaction between the sulfimides and metal contamination, the use of the invention disclosed herein with anaerobic compositions containing organic sulfimides constitutes a highly preferred practice thereof. While the broad class of organic sulfimides can be used successfully, the sulfimides most commonly used can be represented by the formula ##STR5## wherein each of R.sub.8 and R.sub.9 is a hydrocarbon group containing up to about ten carbon atoms, and preferably up to about six carbon atoms. Naturally, R.sub.8 and R.sub.9 can contain any linkage or substituent which does not adversely affect the sulfimide for its intended use in the anaerobic composition. Further, R.sub.8 and R.sub.9 can be united to bond the sulfimide group in a heterocyclic ring, or a polynuclear heterocyclic ring system. Of the organic sulfimides, benzoic sulfimide has been found to be the most preferable. A good combination of shelf stability and cure speed is obtainable with this class of accelerators, but care must be taken in combining sulfimides, particularly benzoic sulfimide, with amines of the types described above. Improper combinations can cause stability problems. However certain selected classes of amines can be used in combination with the sulfimides, and exceptionally good anaerobic compositions can be prepared. A preferred composition is that which contains a sulfimide, particularly benzoic sulfimide, in combination with either a heterocyclic secondary amine as discussed above, or a tertiary N,N-dialkyl aryl amine. Typical amines within the latter class may be represented by the following general formula: ##STR6## wherein E represents a carbocyclic aromatic nucleus selected from the group consisting of phenyl and naphthyl radicals; R.sup.10 and R.sup.11 are lower alkyl radicals of 1 to 4 carbon atoms; t is one of the following: 0, integer equal to from 1 to 5 inclusive; R.sup.12 is a member selected from the groups of lower alkyl and lower alkoxy radicals of 1 to 4 carbon atoms inclusive, provided that when an R.sup.10 radical is in the ortho position, t is greater than 1. For an expanded discussion of this type of system, reference is made to the above mentioned U.S. Pat. No. 3,218,305.

Brief Summary Text (33):

Routine testing easily will determine the optimum amount of accelerator which can be incorporated in a given anaerobic composition. However the following general guide lines may be used. With regard to tertiary amines, large amounts may be used if desired, up to a maximum of about 5 percent by weight of the composition. Most preferably these tertiary amine accelerators are used at from about 1 percent to about 4 percent by weight of the anaerobic composition. The succinimide, phthalimide and formamide accelerators also can be used in significant amounts, up to about 5 percent by weight of the composition, and preferably from about 1 percent to about 5 percent by weight. The sulfimide and secondary amine accelerators generally are used at less than 2 percent by weight of the anaerobic composition. In the special case where a sulfimide is used in combination with a heterocyclic secondary amine or a N,N-dialkyl arylamine, the total of the two components should not exceed about 3 percent by weight of the anaerobic composition.

Brief Summary Text (43):

Generally, chelating agents are categorized by their "donor atoms", e.g., the atoms in the agent which "donate" electron pairs to bind the metal atom into the ring structure. The most common donor atoms in chelating agents are oxygen, nitrogen and sulfur. The

most highly preferred chelating agents are those which utilize a nitrogen atom and an oxygen atom in forming the chelated ring structure. Examples of such chelating agents are ethylenediamine tetraacetic acid, o-aminophenol, and sodium salts of either of these.

Brief Summary Text (44):

Chelating agents other than those having one each of oxygen and nitrogen donor atoms can be used successfully. Typical examples of such compounds are the following: sodium acetylacetonate; polyvinyl alcohol; sodium dimethylglyoximate; sodium salicaldehyde; sodium diethyldithiocarbamate; disodium dithioxaminate; disodium pyrocatecholate; and sodium quinolinolate.

Brief Summary Text (45):

Still another class of treating agents which can be used in the process of this invention to remove metal contamination, is that class of compounds which will react with metal contamination to form metal salts which are insoluble in the anaerobic composition, or its starting materials, as the case may be. Typical treating agents of this class which can be used successfully are as follows: potassium ferricyanate; sodium citrate; sodium pyrophosphate; sodium silicate; disodium oxalate; phosphomolybdic acid; sodium cyanide; sodium stearate; tribasic sodium phosphate; and sodium sulfate.

Detailed Description Text (7):

The treated and untreated portions of the PEGMA were used to prepare anaerobic compositions by adding to each 0.3 percent by weight dimethylparatoluidine, 0.4 percent by weight benzoic sulfimide, 3% by weight cumene hydroperoxide and 50 parts per million by weight quinone. The stability of each formulation then was determined and it was found that the anaerobic composition formulated from the untreated PEGMA was 4 minutes, whereas the composition formulated from the chelator-treated PEGMA was 12 minutes.

Detailed Description Text (14):

An anaerobic composition was prepared from this treated material by adding to it 0.3 percent by weight dimethylparatoluidine and 0.4 percent by weight benzoic sulfimide. The stability of this material was determined and found to be 12 minutes.

Detailed Description Text (16):

Approximately 50 cubic centimeters of dimethylparatoluidine was mixed with 5.6% by weight of the disodium salt of ethylenediamine tetraacetic acid, and agitated in a 250 cubic centimeter glass beaker for 48 hours. Approximately 50 cubic centimeters of cumene hydroperoxide were mixed with 5 percent by weight of the same chelating agent, and agitated in a second beaker for 16 hours. Approximately 50 cubic centimeters of PEGMA containing about 5 percent by weight of benzoic sulfimide were mixed with 5 percent of the same chelating agent and mixed in a third beaker for approximately 16 hours. All three treated materials were allowed to stand over night to permit settling of the chelating agents, following which the treated liquids were removed by decantation.

Detailed Description Text (17):

A sufficient amount of the PEGMA-benzoic sulfimide mixture was added to a portion of the chelator treated PEGMA from Example I to produce a benzoic sulfimide concentration in PEGMA of 0.4 percent by weight. To this was added 0.3 percent by weight of the dimethylparatoluidine treated in this Example, and 3 percent by weight of the cumene hydroperoxide, also treated in this Example. To the final mixture was added 100 parts per million by weight quinone.

Detailed Description Text (24):

A polymerizable acrylate monomer was prepared by reacting two moles of hydroethylmethacrylate with 1 mole of the reaction product of 2 moles of toluene diisocyanate and 1 mole of hydrogenated diphenyldimethylmethane. 100 parts by weight of this monomer were mixed with 50 parts by weight dichloromethane and 15 parts by weight ethylenediamine tetraacetic acid. This mixture was agitated for 72 hours, essentially as described in the preceding Examples. After the chelator had settled, the liquid was removed by decantation and the dichloromethane was allowed to evaporate.

Detailed Description Text (25):

Six percent by weight of the treated acrylate monomer of the preceding paragraph was added to an anaerobic composition essentially identical to those described in Example I (stability 16 minutes). The stability of the final mixture was measured and found to be 19 minutes.

Detailed Description Text (26):

Six percent of the same acrylate monomer which had not been treated as described above in this Example, was added to a portion of the same anaerobic composition described in the preceding paragraph. The stability of this final mixture was measured and found to be eleven minutes.

Detailed Description Text (28):

An anaerobic composition essentially identical to those described in Example I, above, was prepared, except that the level of benzoic sulfimide was increased to 1.6% by weight. The composition immediately was mixed with 5% by weight of ethylenediamine tetraacetic acid and agitated for 18 days.

Detailed Description Text (34):

Three anaerobic formulations were prepared consisting of PEGMA containing three percent by weight cumene hydroperoxide, 0.2 percent by weight benzoic sulfimide, and 0.05 percent by weight dimethylparatoluidine. Formulation A was prepared from the untreated portion of PEGMA, Formulation B from the sulfur treated portion of PEGMA, and Formulation C from the ion exchange resin treated portion of PEGMA. The stabilities of the three Formulations were determined and found to be as follows:

Detailed Description Paragraph Table (3):

	Chelating Agent Stability (Minutes)
	<u>Sodium</u> Acetylacetonate 19 <u>Sodium</u> Salicaldehyde
37 <u>Sodium</u> o-Aminophenolate >75	Disodium Pyrocatecholate 45 <u>Sodium</u> Quinolinolate 36

Detailed Description Paragraph Table (4):

	Chelating Agent Stability (Minutes)
	Polyvinyl Alcohol 70 Disodium Dithioxamidate 32
<u>Sodium</u> Dimethylglyoximate 28 <u>Sodium</u> Diethyldithiocarbamate >75	

Detailed Description Paragraph Table (5):

	Treating Agent Stability (Minutes)
	<u>Sodium</u> Thiosulfate 18 Potassium Ferricyanate 15
<u>Sodium</u> Citrate 19 <u>Sodium</u> Pyrophosphate 28 <u>Sodium</u> Silicate 19 Disodium Oxalate 26 <u>Sodium</u> Cyanide 20 <u>Sodium</u> Stearate 17	

CLAIMS:

1. In a process for preparing an anaerobic adhesive composition, said composition comprising: a free radical polymerizable acrylate ester monomer, the polymerization of which is inhibited by oxygen; and a redox-activated latent initiator of free radical polymerization capable of polymerizing said monomer in the absence of oxygen; the step of reducing the content of metal contamination in said composition which comprises contacting said free radical polymerizable acrylate ester monomer with an insoluble chelating agent, wherein said chelating agent reacts with said metal contamination in said monomer material to form a metal-containing precipitate which is insoluble in said anaerobic adhesive composition, and wherein said anaerobic adhesive composition subsequently possesses an iron content of less than about 0.1 parts per million by weight.
2. The process of claim 1 wherein said anaerobic adhesive composition further comprises a polymerization accelerator comprising an organic sulfimide.

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TITLE: Anaerobic adhesive containing tetrahydroquinoline and benzosulfimideAbstract Text (1):

An adhesive composition which can be applied to various metals and be polymerized and cured upon exclusion from contact with air is disclosed, said composition comprising (1) an anaerobic mixture consisting of a compound represented by the formula ##EQU1## a solvent compound having in the molecule an acrylic or methacrylic group, (2) a small amount of benzosulfimide, (3) tetrahydroquinoline and (4) an organic peroxide.

Brief Summary Text (2):

This invention relates to an anaerobic adhesive composition which can bond various metals, said composition comprising an anaerobic mixture consisting of a polyvalent metal salt of a compound represented by the following general formula ##EQU2## wherein R.sub.1 is a hydrogen atom or methyl group, R.sub.2 is an aliphatic, alicyclic or aromatic polyhydric alcohol residue, and R.sub.3 is an aliphatic, alicyclic

Brief Summary Text (3):

Or aromatic polybasic carboxylic acid residue, and a solvent compound having in the molecule an acrylic or methacrylic group, and incorporated therein, small amounts of benzosulfimide, tetrahydroquinoline and an organic peroxide.

Brief Summary Text (5):

A number of so-called anaerobic adhesives which are polymerized and cured under exclusion from contact with air to exhibit a bonding activity have been known in the art. However, these known anaerobic adhesives have defects and shortcomings such as mentioned below.

Brief Summary Text (6):

In case a curing accelerator is not used in combination, the time required for completion of setting and bonding is extremely long. Further, if metals other than those of iron and copper types are bonded with use of conventional anaerobic adhesives, it generally takes a long time to complete setting and bonding and, in some cases, it is impossible to bond metals. Because of these defects, the application fields of these known anaerobic adhesives are much limited.

Brief Summary Text (7):

In conventional anaerobic adhesives, especially those of the polyether methacrylate type, it is known that tetrahydroquinoline is a strong bonding accelerator together with benzosulfimide acting as an auxiliary accelerator. When tetrahydroquinoline is employed, it is necessary to employ a particular stabilizer such as hydroquinone, 1,4-benzoquinone, hydroquinone monomethyl ether, 2,5-diphenyl-p-benzoquinone in an amount of about 50 to about 600 ppm in proportion to the amount of used tetrahydroquinoline, which results in operational troubles. Further, anaerobic adhesives formed by incorporation of these stabilizers are defective in that they are darkly colored or the bonding speed differs among lots.

Brief Summary Text (9):

The effects attained by the anaerobic adhesive composition of this invention are as follows:

Brief Summary Text (15):

This invention is to provide an anaerobic adhesive composition having a high bonding property.

Brief Summary Text (16):

More specifically, in accordance with this invention, there is provided an anaerobic adhesive composition which has a quick setting property and can bond tightly not only metals of copper and iron types but also other various metals, said composition comprising an anaerobic mixture containing a polyvalent metal salt of a compound represented by the following general formula [1] ##EQU3## and incorporated therein, small amounts of an organic peroxide as a curing catalyst, tetrahydroquinoline as a curing accelerator and stabilizer and benzosulfimide as a promoter.

Brief Summary Text (17):

It is quite surprising that in this invention tetrahydroquinoline has good activities not only as an accelerator but also as a stabilizer, through a compound of the general formula [1] is the polyester methacrylate type.

Brief Summary Text (18):

The reason why in the anaerobic adhesive composition of this invention tetrahydroquinoline acts effectively not only as an accelerator but also as a stabilizer has not completely been elucidated, but it is surmised that high synergetic effects can be attained by tetrahydroquinoline and the metal salt contained in the anaerobic mixture of this invention.

Brief Summary Text (20):

A metal salt of the compound of the general formula [1] acts effectively as a stabilizer when used in combination with tetrahydroquinoline in the anaerobic adhesive composition of this invention. Moreover, incorporation of this metal salt imparts to the resulting adhesive composition such properties that the composition can bond various metals and can bond even an oil coated surface tightly and promptly without use of a primer.

Brief Summary Text (22):

As specific examples of the compound represented by the general formula [1], there can be mentioned ethyleneglycol methacrylate phthalate, propyleneglycol methacrylate phthalate, ethyleneglycol methacrylate succinate, propyleneglycol methacrylate succinate, propyleneglycol methacrylate hexahydrophthalate, a partially esterified product of succinic acid anhydride with bis-phenol dihydroxyethyl ether monomethacrylate and a partially esterified product of phthalic anhydride with hydrogenated bis-phenol A monomethacrylate.

Brief Summary Text (23):

As regards the synthesis of these compounds, it is advantageous to subject a partial esterification reaction of a partial methacrylate of polyhydric alcohol with a polybasic carboxylic acid anhydride. Various method can be adopted for the synthesis of compounds of the general formula [1], and according to any method, they can be prepared with ease on an industrial scale at a low cost.

Brief Summary Text (28):

c. Methacrylates and acrylates of polyhydric alcohols.

Brief Summary Text (29):

d. Polyester methacrylates and polyester acrylates.

Brief Summary Text (31):

f. Epoxy methacrylates and epoxy acrylates.

Brief Summary Text (32):

As specific examples of the compound of the type (c), there can be mentioned ethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate, trimethylolpropane monomethacrylate, trimethylolpropane trimethacrylate, and corresponding acrylates.

Brief Summary Text (34):

As specific examples of the compound of the type (e), there can be mentioned an adduct of a monomethacryloyloxypropyl ester of phthalic or succinic acid and glycidyl methacrylate, and an adduct of a monomethacryloyloxypropyl ester of phthalic or succinic acid and propylene oxide.

Brief Summary Text (37):

Various polyvalent metals can be used for formation of polyvalent metal salts of the compound of the general formula [1], but use of divalent metals such as calcium,

magnesium and zinc is especially preferred. In view of the reactivity, the solubility and the like, it is preferred that metal oxides and hydroxides such as $\text{Ca}(\text{OH})_2$, CaO , $\text{Mg}(\text{OH})_2$, MgO , $\text{Zn}(\text{OH})_2$ and the like be used for formation of the polyvalent metal salt of the compound of the general formula [1].

Brief Summary Text (38):

In this invention, benzosulfimide acting as an auxiliary bonding accelerator is used in an amount of about 0.01 to about 5% by weight, preferably 0.1 to 1.0% by weight, based on the anaerobic mixture. Although other amides and imides such as succinimide, phthalimide and formamide are effective as auxiliary accelerators, they are inferior to benzosulfimide with respect to the setting rate. If benzosulfimide is not at all incorporated, the bonding rate is extremely low and the resulting composition has no practical utility as an adhesive.

Brief Summary Text (39):

It is preferred that the amount of tetrahydroquinoline acting as an accelerator and stabilizer is 0.5 to 3 times, especially 1 to 2 times, the amount used of benzosulfimide i.e. 0.005 to 15% by weight of the mixture. It must be noted that when the amount of benzosulfimide is larger than the amount of tetrahydroquinoline, it sometimes happens that the storage stability of the resulting composition is degraded.

Brief Summary Text (40):

As the organic peroxide to be added as a curing agent, hydroperoxides such as tertiary butyl hydroperoxide, cumene hydroperoxide, di-isopropylbenzene hydroperoxide and p-menthane hydroperoxide are most effective, and ketone peroxides, dialkyl peroxides and peroxy esters can also be employed in some cases. A mixture of two or more of these organic peroxides can also be employed effectively. The organic peroxide is generally incorporated in an amount of about 0.1 to about 10% by weight based on the anaerobic mixture, but in some special cases the amount of the organic peroxide can be reduced below 0.1% by weight. However, if the organic peroxide is used in an amount exceeding 10% by weight, the excessive peroxide acts merely as a diluent and does more harm than good.

Brief Summary Text (44):

Further, the adhesive composition of this invention can without use of primer, tightly and promptly bond materials that can hardly be bonded with conventional anaerobic adhesives, such as materials plated with such a metal as nickel, chromium and zinc, stainless steels, oil coated surfaces and the like.

Brief Summary Text (45):

In addition to the above-mentioned indispensable ingredients, the anaerobic adhesive composition of this invention may further comprise plasticizers such as di-n-butyl phthalate, dimethyl sebacate and tricresyl phosphate, thickeners such as silica, alumina and organic soluble polymers, dyes, UV absorbers and the like.

Detailed Description Text (4):

A four-neck flask equipped with a stirrer, an air condenser and a thermometer was charged with 152 parts of 2-hydroxypropyl methacrylate, 40 parts of succinic anhydride and 5 parts of triethylbenzyl ammonium chloride, and the mixture was heated and agitated at 90.degree.C. for 3 hours. Then, 27 parts of glycidyl methacrylate was gradually added to the reaction mixture, and reaction was further continued at 90.degree.C. for 3 hours to obtain a light-yellow, transparent, viscous liquid having an acid value of 68. This liquid product was incorporated with 30% by weight of 2-hydroxypropyl methacrylate as the solvent compound and with magnesium oxide in an amount of 70% of the theoretical amount necessary for neutralization, and the mixture was reacted at 70.degree.C. for 4 hours to obtain a light-yellow, transparent, lowly viscous mixture of an anaerobic compound containing a magnesium salt thereof (hereinafter referred to as "anaerobic mixture [A]").

Detailed Description Text (7):

The light-yellow, transparent liquid of an acid value of 68 obtained in Example 1 was incorporated with 30% by weight of 2-hydroxypropyl methacrylate as the solvent compound and with calcium oxide as the neutralizer in an amount of 70% of the theoretical amount necessary for neutralization, and the mixture was reacted at 70.degree.C. for 3 hours to obtain a light-yellow, transparent, lowly viscous anaerobic mixture [B] containing a calcium salt.

Detailed Description Text (10):

A four-neck flask equipped with the same devices as used in Example 1 was charged with

156 parts of 2-hydroxypropyl methacrylate, 59 parts of phthalic anhydride and 5.5 parts of triethylbenzyl ammonium chloride, and the mixture was reacted at 90.degree.C. for 3 hours. Then, 21 parts of glycidyl methacrylate was gradually added to the reaction mixture, and reaction was carried out at 90.degree.C. for 3 hours to obtain a light-yellow, transparent, viscous liquid having an acid value of 67. The so obtained liquid was incorporated with 30% by weight of 2-hydroxypropyl methacrylate as the solvent compound and with zinc hydroxide in an amount of 70% of the theoretical amount necessary for neutralization, and the mixture was reacted at 70.degree.C. for 4 hours to obtain a light-yellow, transparent, lowly viscous anaerobic mixture [C] containing a zinc salt.

Detailed Description Text (13):

A four-neck flask equipped with the same devices as used in Example 1 was charged with 75 parts of 2-hydroxypropyl methacrylate, 31 parts of hexahydrophthalic anhydride and 2.8 parts of triethylbenzyl ammonium chloride, and the mixture was reacted at 90.degree.C. for 2 hours. Then, 12 parts of glycidyl methacrylate was gradually added dropwise to the reaction mixture, and reaction was carried out at 90.degree.C. for 2 hours to obtain a light-yellow, transparent, viscous liquid having an acid value of 66. The so obtained liquid was incorporated with 30% by weight of 2-hydroxypropyl methacrylate as the solvent compound and with zinc hydroxide in an amount of 70% of the theoretical amount necessary for neutralization, and the mixture was reacted at 80.degree.C. for 4 hours to obtain a light-yellow, transparent, lowly viscous anaerobic mixture [D] containing a zinc salt.

Detailed Description Text (15):

An anaerobic adhesive (a) was prepared from the components given below, and physical properties were determined to obtain results shown in Table 1.

Detailed Description Text (16):

It was found that the anaerobic adhesive composition (a) exhibited a good bonding property to a zinc plating which could hardly be bonded by any of commercially available products. Further, the anaerobic adhesive (a) showed a considerable quicksetting property in comparison with commercially available products.

Detailed Description Text (18):

The gelation time of the anaerobic adhesive (a) of this invention was more than 100 minutes at 82.degree.C. and was more than 1 month at 50.degree.C. In conventional anaerobic adhesives, if the gelation time is more than 30 minutes at 82.degree.C., it is construed that the adhesives are stable for more 6 months to 1 year at room temperature. In view of the foregoing, it will readily be understood that the anaerobic adhesive of this invention is very stable though it has a quick-setting property.

Detailed Description Text (20):

The following anaerobic adhesive (b) and (c) were prepared and their physical properties were determined according to the method described in Example 5 to obtain results shown in Table 2, from which it is seen that each of them had excellent properties.

Detailed Description Text (22):

In the composition of the anaerobic adhesive (a), the amount of 1,2,3,4-tetrahydroquinoline was changed within a range of 0.5 to 1.5% by weight while using benzosulfimide in an amount of 0.5% by weight, and the stability to gelation was determined with respect to each of obtained anaerobic adhesives to obtain results shown in Table 3, from which it is seen that 1,2,3,4-tetrahydroquinoline has a good stabilizing activity to gelation. In this test, no change of the physical properties such as the setting time and the fracture torque was brought about by the change in the amount incorporated of 1,2,3,4-tetrahydroquinoline.

Detailed Description Text (24):

In the composition of the anaerobic adhesive (a), instead of 1,2,3,4-tetrahydroquinoline, other tertiary amines indicated in Table 4 were employed, and the stability was determined with respect to each of the resulting adhesives to obtain results shown in Table 4, from which it is seen that 1,2,3,4-tetrahydroquinoline is most effective.

Detailed Description Text (26):

The anaerobic adhesive (a) was incorporated with 100 ppm of polymerization inhibitor indicated in Table 5, and the physical properties were determined to obtain results shown in Table 5, from which it is seen that incorporation of a polymerization

inhibitor is quite unnecessary in the anaerobic adhesive composition of this invention.

Detailed Description Text (28):

An anaerobic compound indicated in Table 6, which was free of such a polyvalent metal salt as used in this invention, was incorporated with 0.5% by weight of benzosulfimide, 1.0% by weight of 1,2,3,4-tetrahydroquinoline and 3.0% by weight of cumene hydroperoxide, and the stability as the anaerobic adhesive was examined to obtain results shown in Table 6. As is seen from these results, in each case gelation was caused to occur at room temperature before it was tested at 82.degree.C. Thus, it will readily be understood that the polyvalent metal salt used in this invention has a very effective activity as a gelation stabilizer.

Detailed Description Paragraph Table (1):

Composition of Anaerobic Adhesive (a): Anaerobic mixture [A] 30 parts Anaerobic mixture [C] 10 parts 1,2,3,4-Tetrahydroquinoline 0.4 part Benzosulfimide 0.2 part Cumene hydroperoxide 1.2 parts

Detailed Description Paragraph Table (3):

Composition of Anaerobic Adhesive (b): Anaerobic mixture [B] 30 parts Anaerobic mixture [C] 10 parts 1,2,3,4-Tetrahydroquinoline 0.4 part Benzosulfimide 0.2 part Cumene hydroperoxide 1.2 parts Composition of Anaerobic Adhesive (c): Anaerobic mixture [D] 40 parts 1,2,3,4-Tetrahydroquinoline 0.4 part Benzosulfimide 0.2 part Cumene hydroperoxide 1.2 parts

Detailed Description Paragraph Table (4):

Table 2	Physical Properties				Anaerobic	Anaerobic
Adhesive (b)	Adhesive (c)				Gelation time at	
82.degree.C.	more than 100	more than 100	minutes	minutes	Gelation time at 50.degree.C.	
more than 1	more than 1	month	month	Zinc-plated bolt and nut	Setting time (min)	150 130
Fracture torque (Kg-cm)	230	280	Iron bolt and nut	Setting time (min)	20	13
Fracture torque (Kg-cm)	410	320				

Detailed Description Paragraph Table (8):

Table 6	Anaerobic Compound	Gelation Time (min)
at 82.degree.C.	Ethyleneglycol dimethacrylate	0
Diethyleneglycol dimethacrylate	0	Polyethyleneglycol dimethacrylate
0	2-Hydroxyethyl methacrylate	0
2-Hydroxypropyl methacrylate	0	5% by weight of anaerobic compound of this invention and 95% by weight more than 100 of polyethyleneglycol dimethacrylate

CLAIMS:

1. An anaerobic adhesive composition comprising an anaerobic mixture consisting of (a) at least one polyvalent metal salt of a carboxylate compound of the formula ##EQU4## wherein R.sub.1 is hydrogen or methyl, R.sub.2 is an aliphatic, alicyclic or aromatic polyhydric alcohol residue, and R.sub.3 is an aliphatic, alicyclic or aromatic polybasic carboxylic acid residue,

(b) a solvent compound having in its molecule an acrylic or methacrylic group, and (c) from 0.01 to 5%, by weight of the mixture, of benzosulfimide, from 0.1 to 10%, by weight of the mixture, of an organic peroxide and from .005 to 15%, by weight of the mixture, of a tetrahydroquinoline.

2. An anaerobic adhesive composition according to claim 1 wherein the polyvalent metal is calcium, magnesium or zinc.

3. An anaerobic adhesive composition according to claim 1 wherein the carboxylate compound is ethyleneglycol methacrylate, phthalate, propyleneglycol methacrylate phthalate, ethyleneglycol methacrylate succinate, propyleneglycol methacrylate succinate, propyleneglycol methacrylate hexahydrophthalate, a partially esterified product of a monomethacrylate of bis-phenol dihydroxyethyl ether and succinic anhydride, or a partially esterified product of a monomethacrylate of hydrogenated bis-phenol A and phthalic anhydride.

4. An anaerobic adhesive composition according to claim 1 wherein the solvent compound is selected from the group consisting of (a) alkyl esters of methacrylic acid and acrylic acid, (b) hydroxyalkyl esters of methacrylic acid and acrylic acid, (c) methacrylates and acrylates of polyhydric alcohols, (d) polyester methacrylates and

polyester acrylates, (e) said carboxylate compound and adducts of said carboxylate compound and epoxy compounds, and (f) epoxy methacrylates and epoxy acrylates.